

Inorganic chemistry

Lecturer • 11

Valence Bond Theory

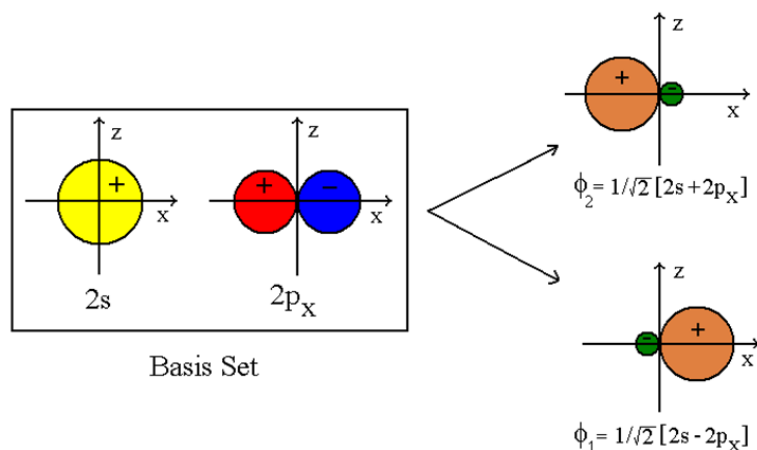
- Extends the Lewis concept of electron pair bonds by introducing the notion of orbital overlap and hybridization.
- Hybridization is necessary to account for molecular geometry predicted by VSEPR
- Hybrid atomic orbitals are constructed by making linear combinations (sums and differences) between hydrogen-like orbitals in the valence shell of each atom

Hybridization

- Example: BeH_2
- Linear Molecule, equivalent Be-H bonds
- Symmetry Adapted Linear Combination (SALC) of hydrogen-like atomic orbitals in the valence shell of Be
- Basis set consists of: $2s$, $2p_x$, $2p_y$, $2p_z$
- Only $2s$ and $2p_x$ are mixed; $2p_y$ and $2p_z$ retain their original form.
- “ideal” hybrids $\frac{1}{2} s$, $\frac{1}{2} p$ character
- Energetic “cost” of hybridization (promotion energy) is offset by formation of stronger bonds

A summary of hybrid orbitals, valence bond theory, VSEPR, resonance structures, and octet rule.				
Linear	Trigonal planar	Tetrahedral	Trigonal bipyramidal	Octahedral
sp	sp^2	sp^3	dsp^3	d^2sp^3
BeH_2	BH_3	CH_4	PF_5	SF_6
BeF_2	BF_3	CF_4	PCl_5	IOF_5
CO_2	CH_2O	CCl_4	PFCl_4	PF_6^-
HCN	$(>\text{C}=\text{O})$	CH_3Cl	$:\text{SF}_4$	SiF_6^{2-}
$\text{HC}\equiv\text{CH}$	$>\text{C}=\text{C}<$	NH_4^+	$:\text{TeF}_4$	$:\text{BrF}_5$
	CO_3^{2-}	$:\text{NH}_3$	$::\text{ClF}_3$	$:\text{IF}_5$
	benzene	$:\text{PF}_3$	$::\text{BrF}_3$	$::\text{XeF}_4$
	graphite	$:\text{SOF}_2$	$:::\text{XeF}_2$	
	fullerenes	$::\text{OH}_2$	$:::\text{I}_3^-$	
	$\bullet\text{NO}_2$	$::\text{SF}_2$	$(:::\text{I I}_2^-)$	
	N_3^-		$:::\text{ICl}_2^-$	
	$:\text{OO}_2 (\text{O}_3)$	SiO_4^{4-}		
	$:\text{SO}_2$	PO_4^{3-}		
	SO_3	SO_4^{2-}		
		ClO_4^-		
• a lone odd electron : a lone electron pair				

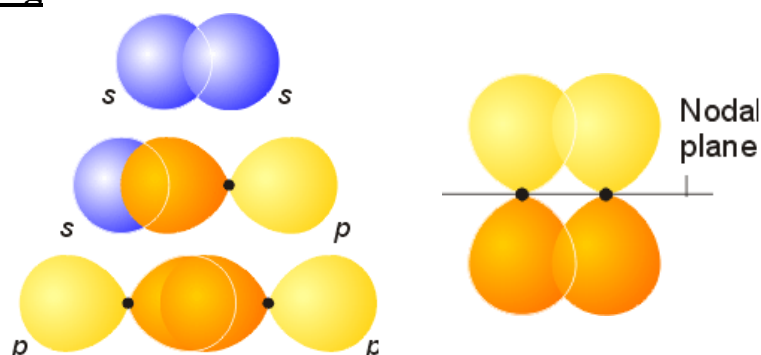
sp hybridization



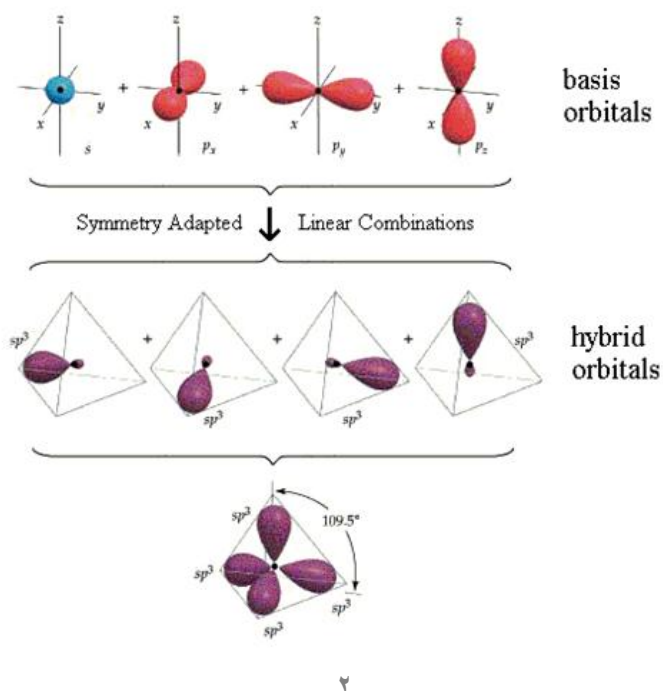
Bonding Description

- Valence electrons of each atom are distributed among the available orbitals.
- In this case, the two valence electrons of Be are placed in the sp hybrid orbitals; the remaining p orbitals are vacant.
- Each H atom has one electron in the $1s$ orbital.
- Orbitals of each atom overlap to form electron pair bonds.

Sigma and Pi Bonding



sp³ hybridization



VBT description of H₂O

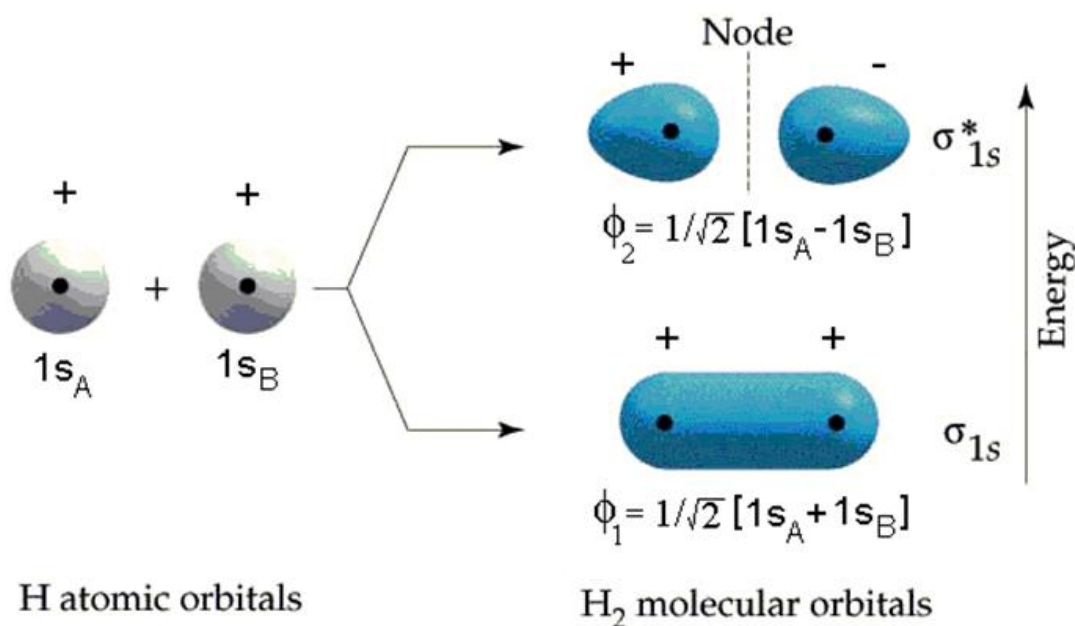
- Oxygen has sp³ hybridization
- Ideal tetrahedral angle is 109.5°
- Observed bond angle in H₂O is ~ 105°
- This indicates that hybrids involved in O-H bonding orbitals have more p-character
- Lone-pair orbitals on oxygen have more s-character

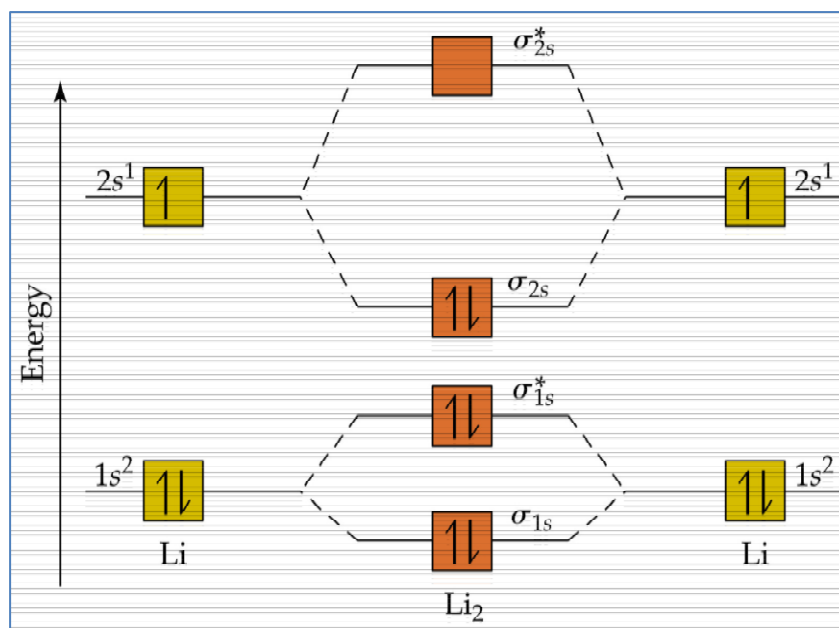
Molecular Orbital Theory

- Fundamentally different than VBT
- Valence atomic orbitals of all atoms in the molecule form the basis set
- For convenience, orbitals on symmetry-related atoms are combined into symmetry-adapted linear combinations called ligand group orbitals (LGOs)
- Atomic orbitals on central atom are mixed with LGOs to generate molecular orbitals (MOs)
- In the final step, valence electrons are placed into MOs starting at lowest energy

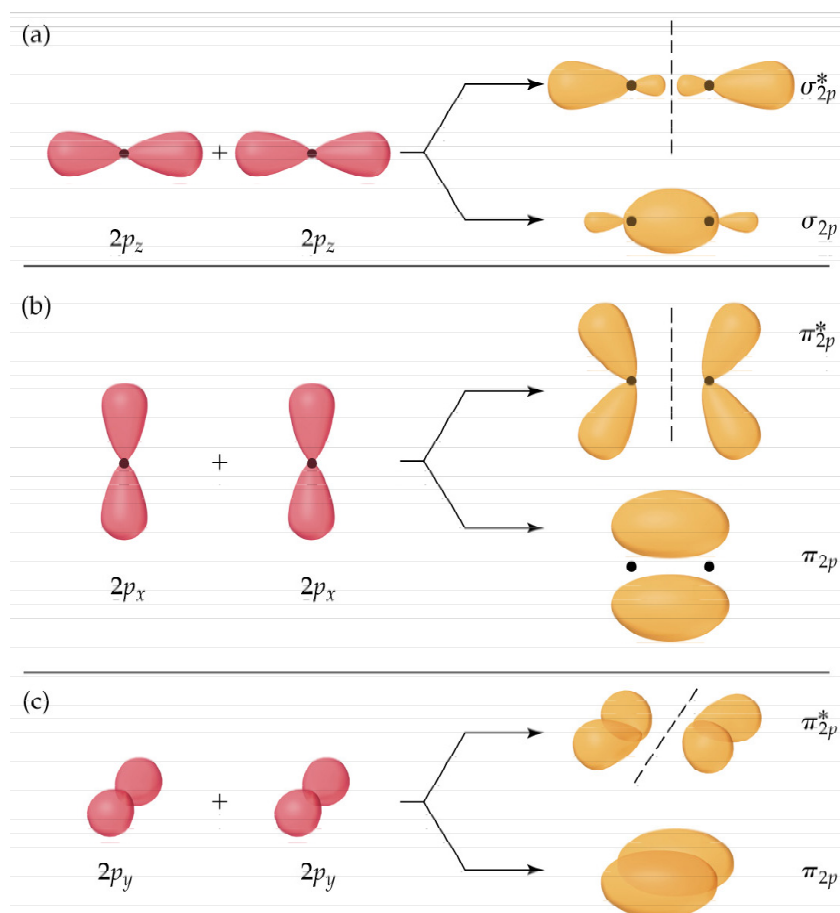
Molecular Orbitals of H₂

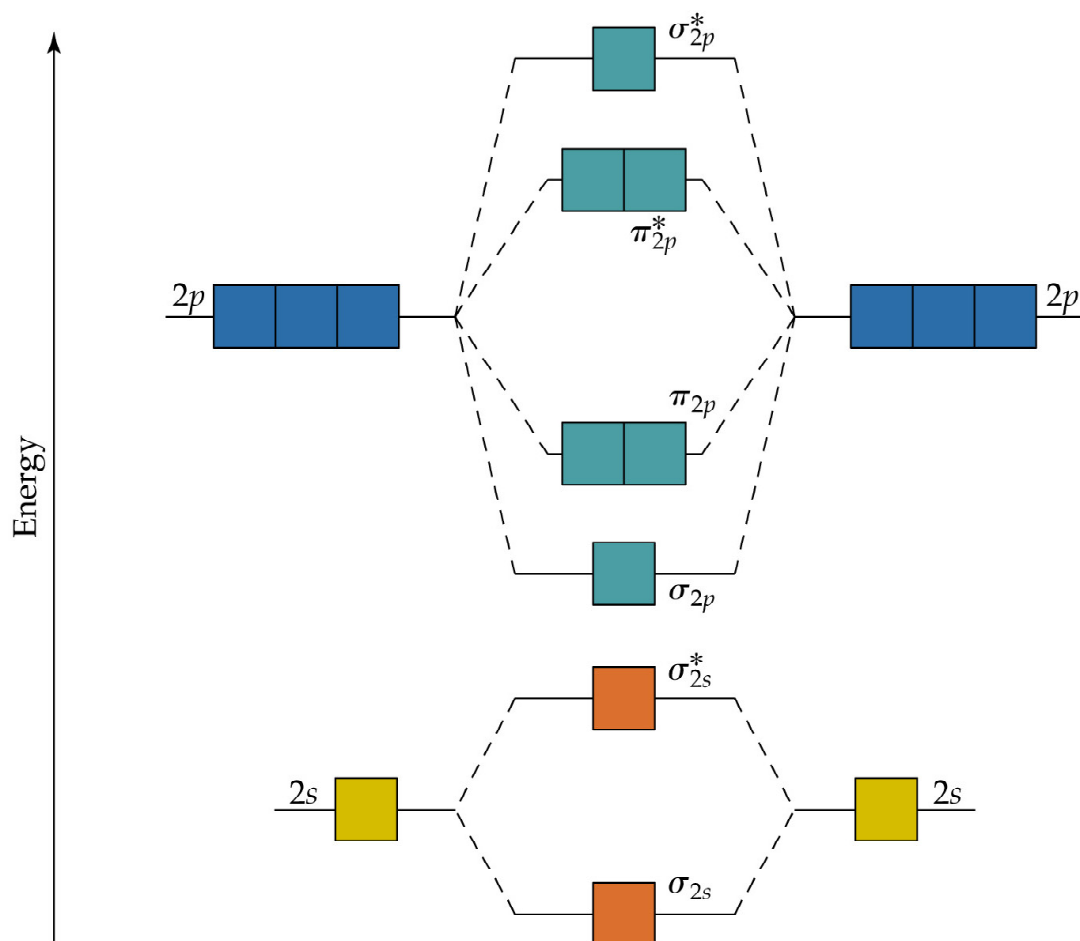
- Basis set of orbitals consists of only the 1s orbital on each H-atom
- Linear combinations of these orbitals produce two molecular orbitals
- + combination gives bonding orbital σ(1s) (constructive interference between wavefunctions)
- - combination gives antibonding orbital σ*(1s) (destructive interference)

Molecular Orbitals of H₂

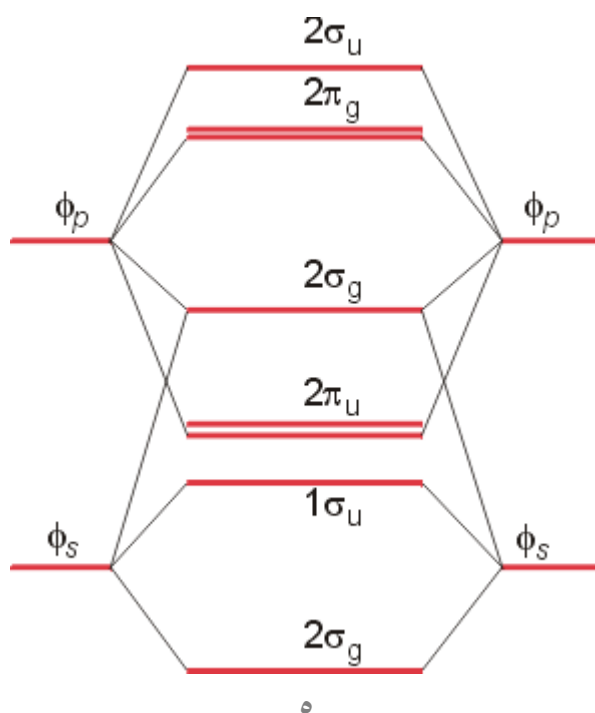
Molecular Orbitals of Li_2 

NOTE: Both bonding and antibonding orbitals arising from the $1s$ orbitals are filled – no net bonding results from core electrons!

p-Orbital overlap modes

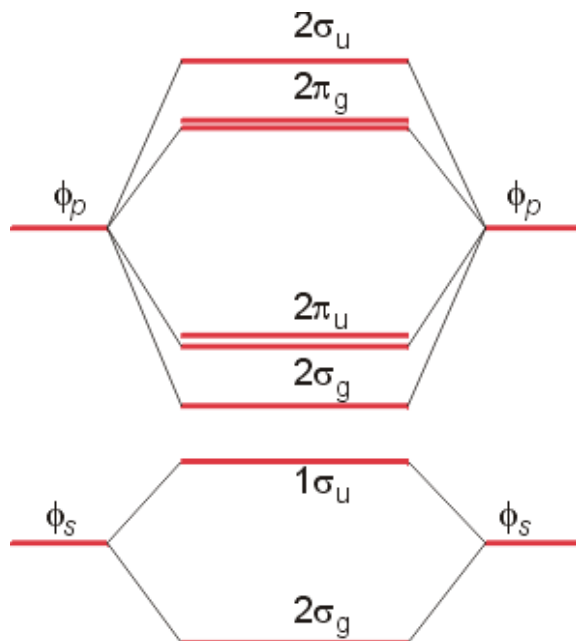
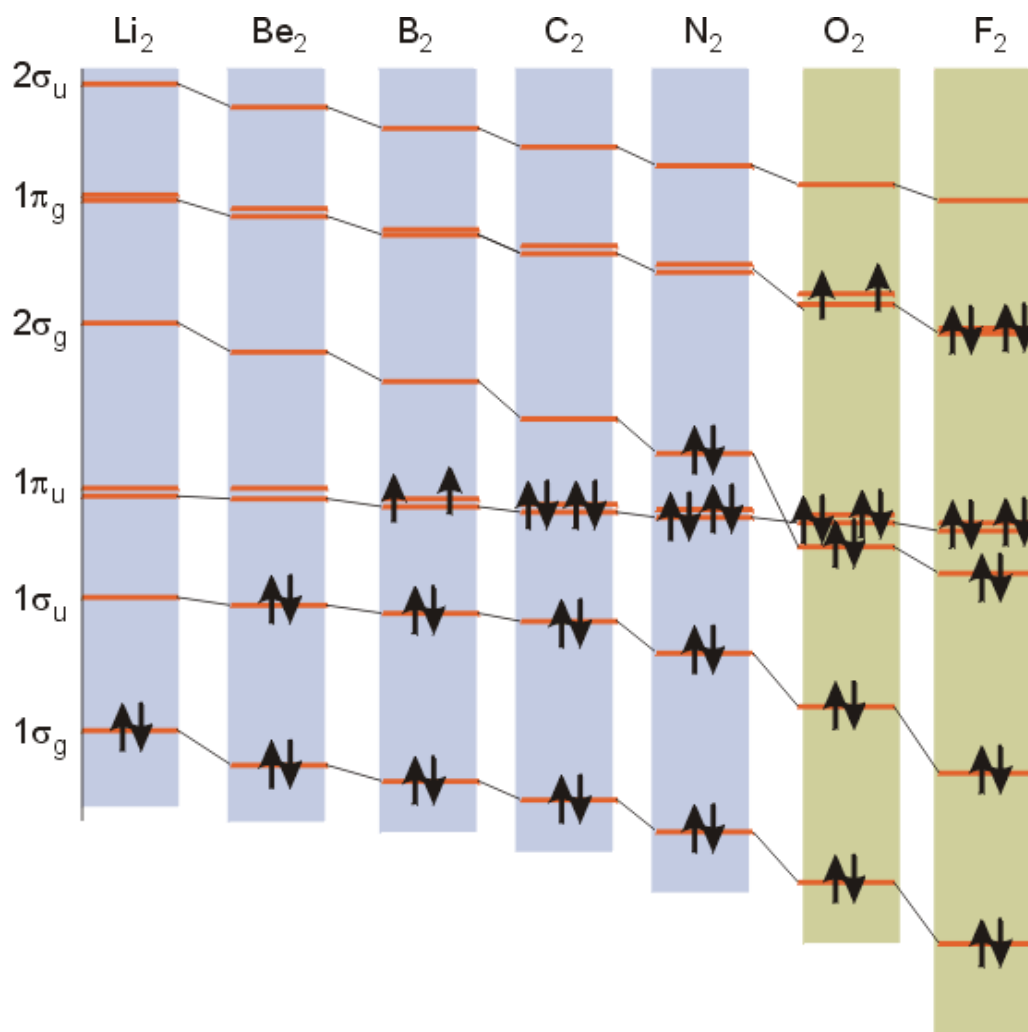
Homonuclear Diatomic with p-OrbitalsEffect of s-p interaction

For atoms early in the 2nd period, energy separation between 2s and 2p orbitals is small. This allows mixing of s(2s) and s(2p) orbitals that raises the energy of the s(2p) orbital above that of the p(2p) .



MO diagram for O_2 and F_2

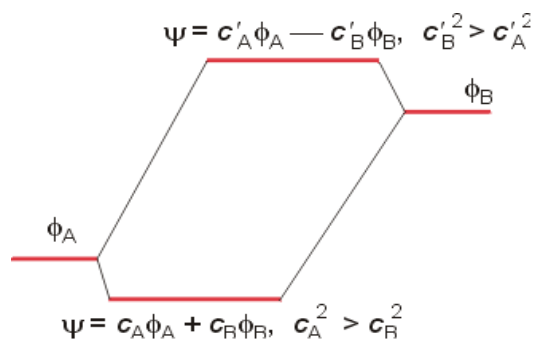
Later in the period, the energy separation of the 2s and 2p orbitals is greater (decreasing s-p interaction), so $s(2p)$ drops below $p(2p)$.

Molecular Orbital diagrams for 2nd row diatomics

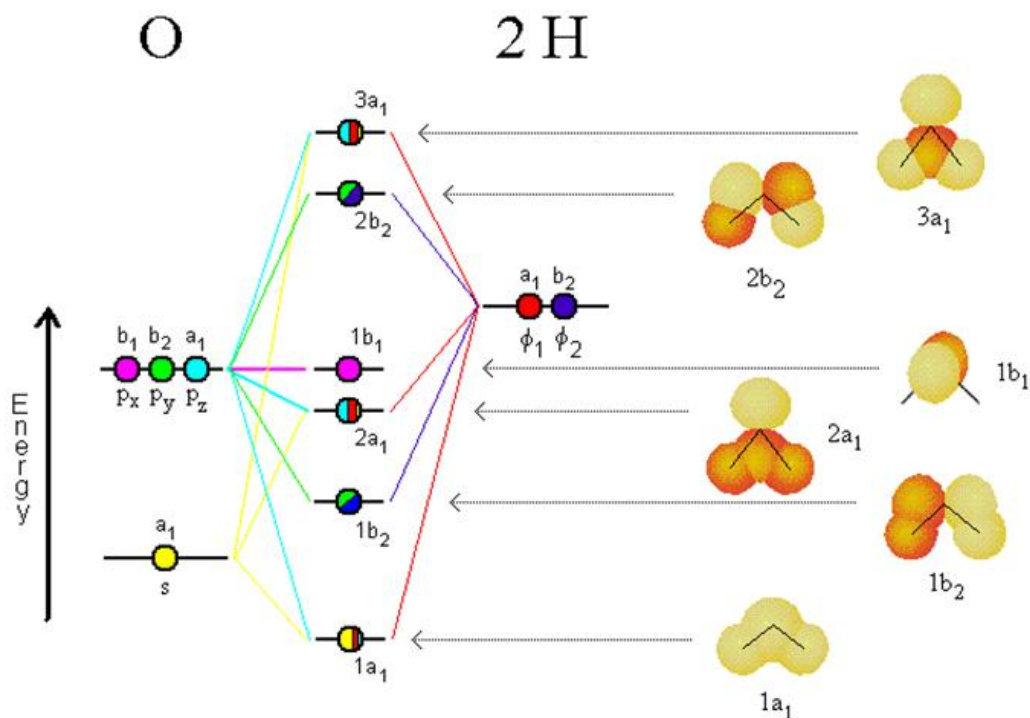
Heteronuclear Diatomics

Strength of orbital interactions depends upon:

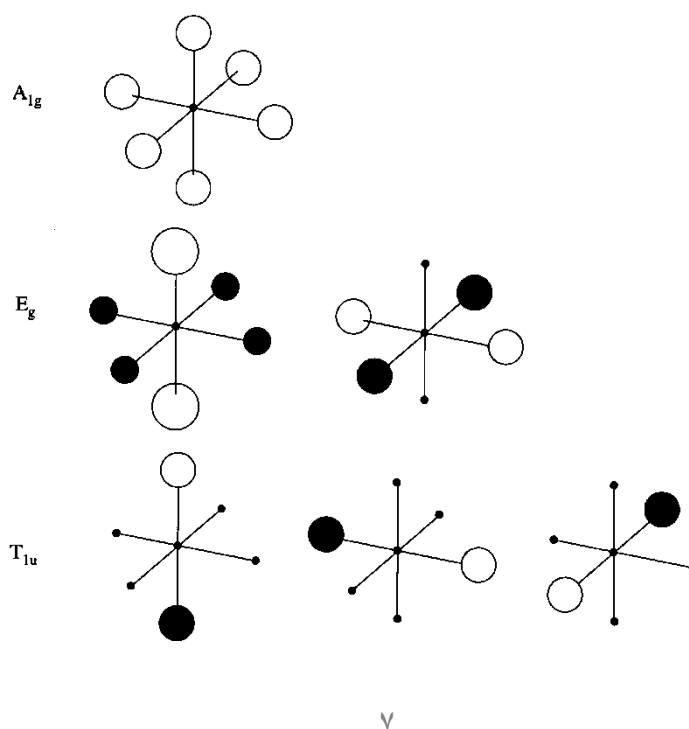
- Symmetry match
- Spatial overlap
- Energy overlap

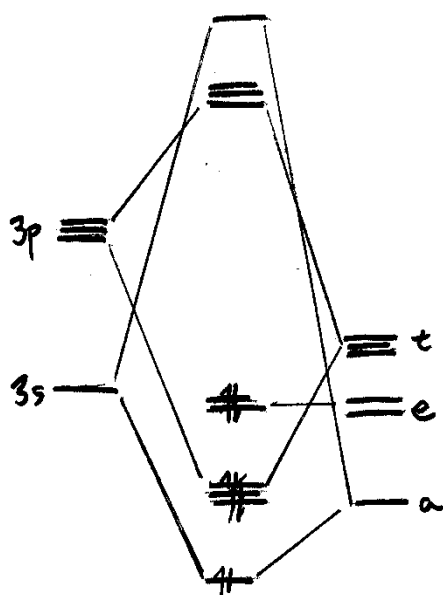
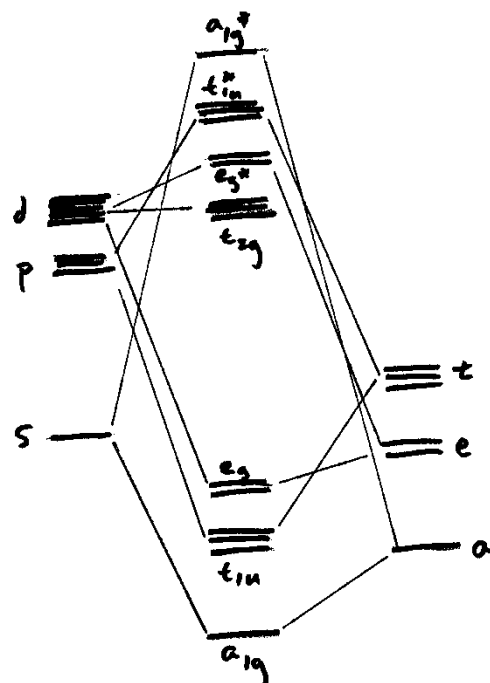


Molecular Orbitals of Water

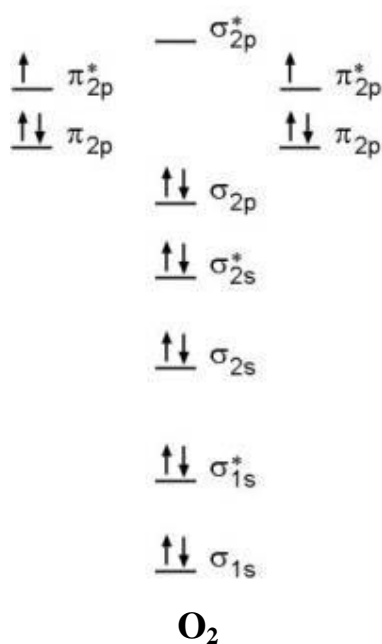


Fluorine SALCs for SF_6

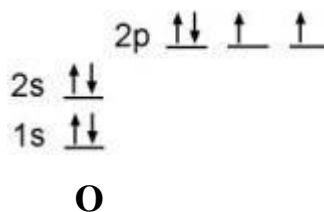


MO diagram for SF₆no d-orbitalswith d-orbitalsMolecular Orbital Theory

The goal of molecular orbital theory is to describe molecules in a similar way to how we describe atoms, that is, in terms of orbitals, orbital diagrams, and electron configurations. For example, to give you a glimpse at where we are headed, the following are orbital diagrams for O₂ and O.



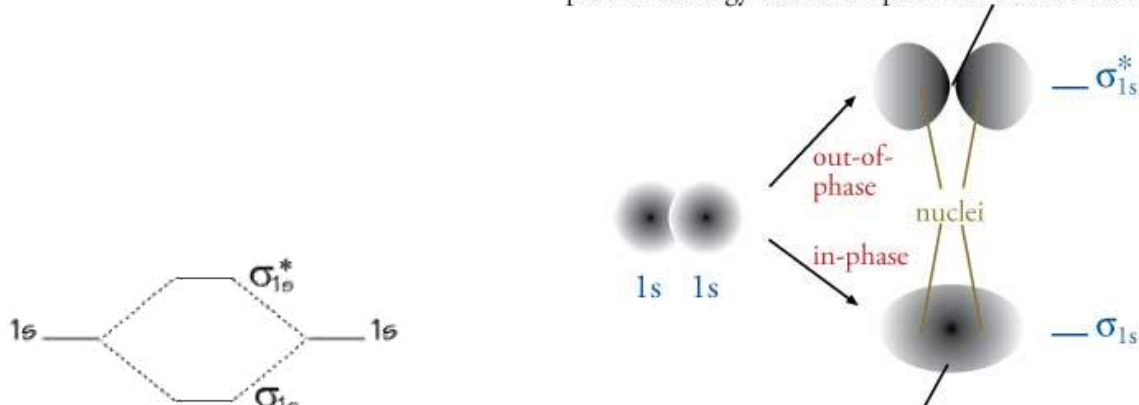
- Each line in the molecular orbital diagram represents a molecular orbital.



The following diagram shows the bonding and antibonding molecular orbitals formed from the interaction of two 1s atomic orbitals.

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Decreased negative charge between the nuclei leads to decreased attractions between the negative charge from the electrons and the positively charged nuclei. This makes the sigma 1s antibonding molecular orbital higher potential energy than the separate 1s atomic orbitals.



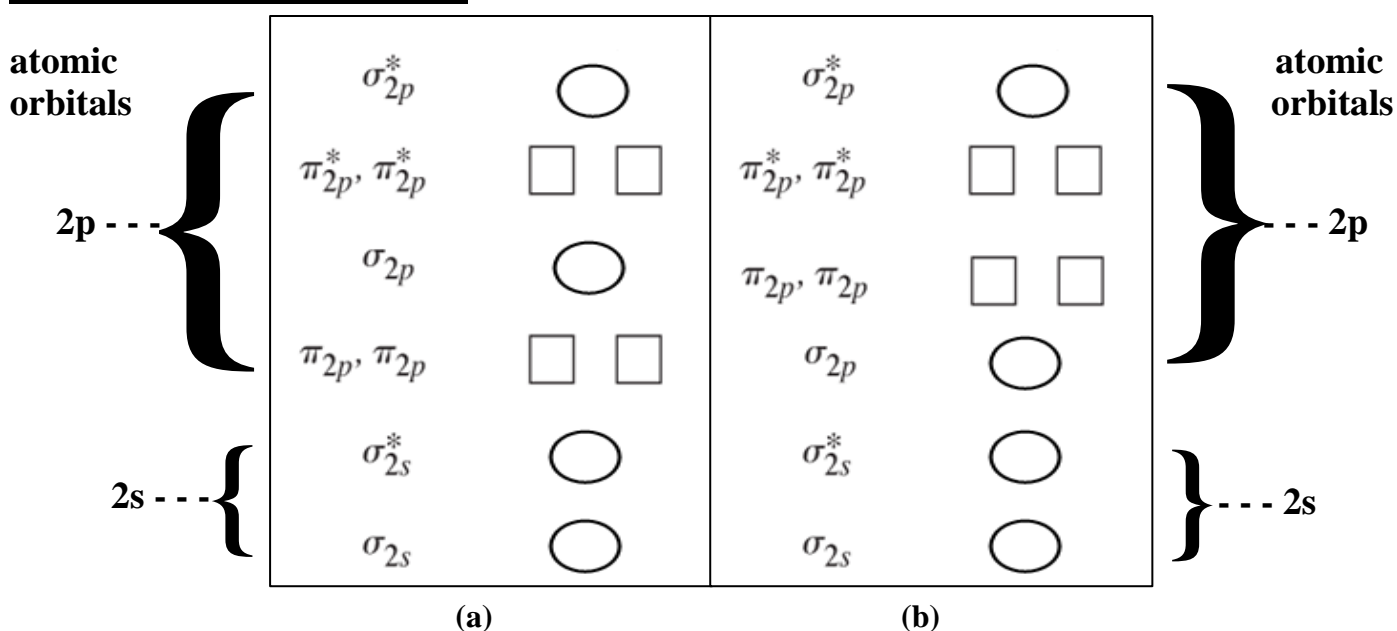
Increased negative charge between the nuclei leads to increased attractions between the negative charge from the electrons and the positively charged nuclei. This makes the sigma 1s bonding molecular orbital lower potential energy than the separate 1s atomic orbitals.

When two larger atoms combine to form a diatomic molecule (like O_2 , F_2 , or Ne_2), more atomic orbitals interact. The LCAO approximation assumes that only the atomic orbitals of *about* the same energy interact. For O_2 , F_2 , or Ne_2 , the orbital energies are different enough so only orbitals of the *same* energy interact to a significant degree.

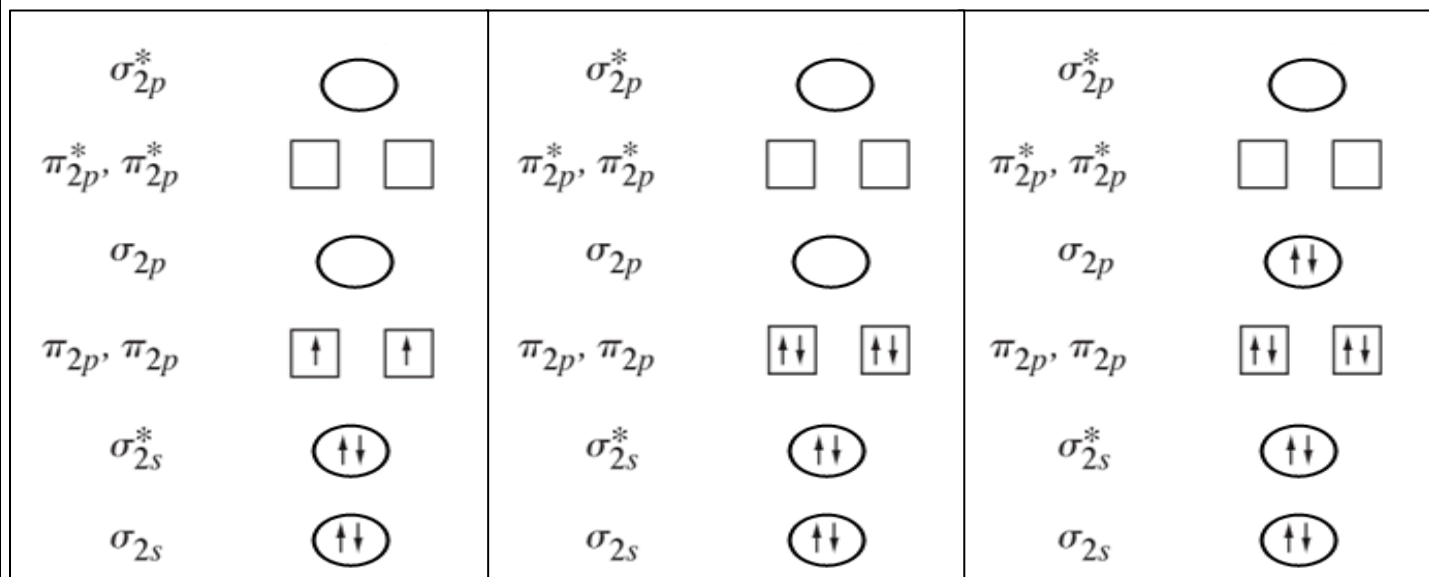
Molecular Orbital Theory

To illustrate the aufbau process for these molecular orbitals, we will consider the homonuclear diatomic molecules of the second-period elements (molecules formed from two atoms of the same second-period element).

There are two aufbau orders



For these molecules. The first order (a) pertains to the molecules Li_2 to N_2 . the second order (b) is the order for O_2 and F_2 .

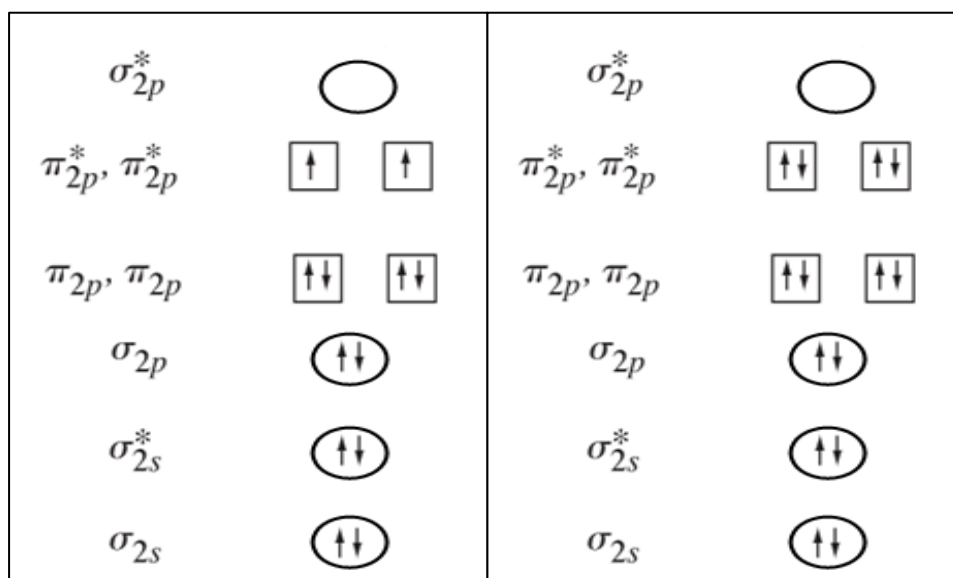


B_2

C_2

N_2

- Molecular orbital energy-level diagrams for B_2 , C_2 , and N_2 .

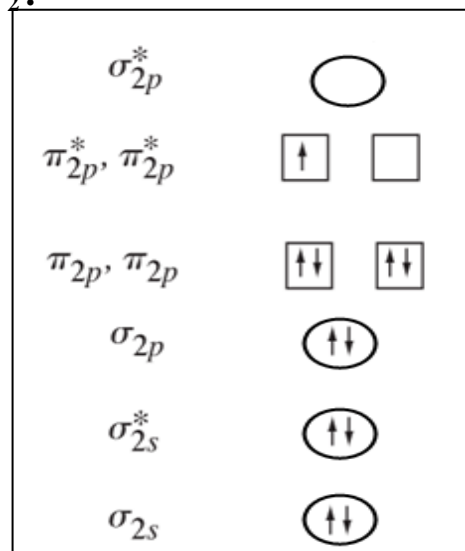


O_2

F_2

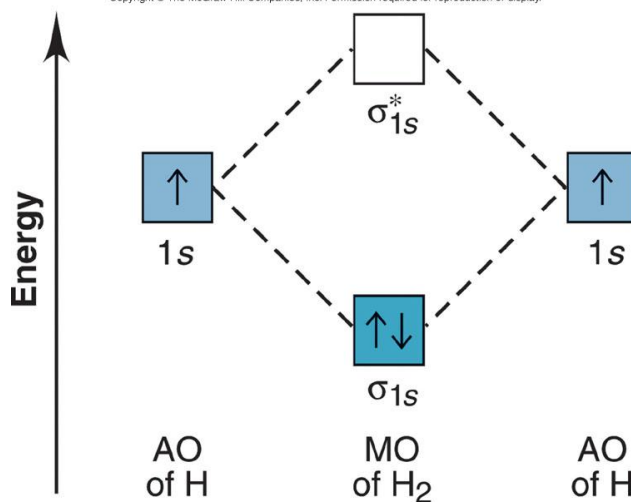
- Molecular orbital energy-level diagrams for O_2 and F_2 .

- Molecular orbital energy-level diagrams for NO .



Molecular orbital diagram for the H₂ molecule

MOs are filled in the same sequence as for AOs (aufbau and exclusion principles, Hund's rule)



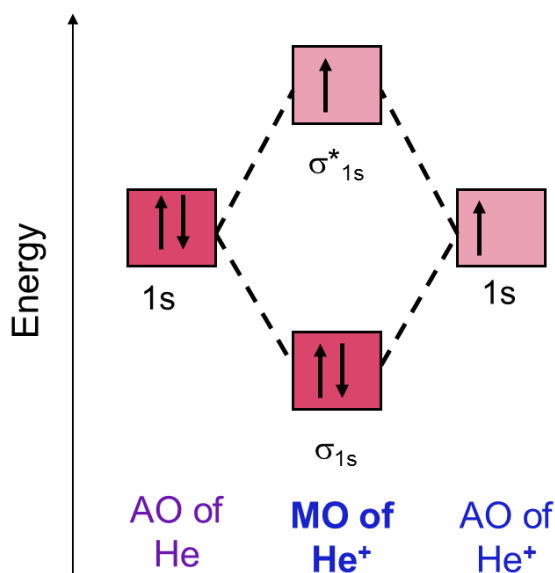
$$\text{H}_2 \text{ bond order} = \frac{1}{2}(2 - 0) = 1$$

The MO bond order

$[\frac{1}{2} (\text{no. of } e^- \text{ in bonding MOs}) - (\text{no. of } e^- \text{ in antibonding MOs})]$
 higher bond order = stronger bond

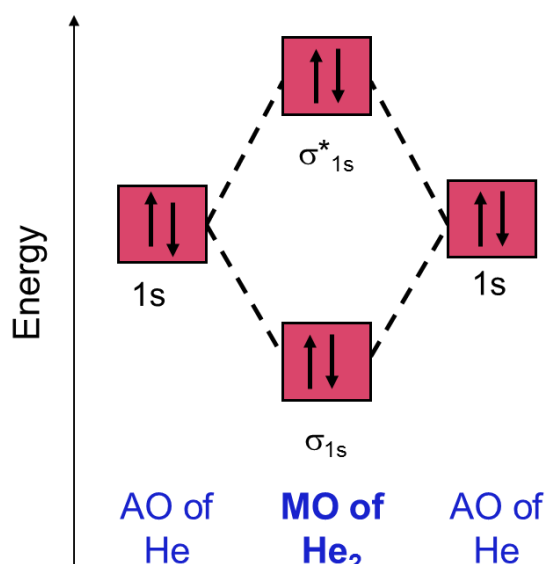
Has predictive power!

MO diagrams for He₂⁺ and He₂



He₂⁺ bond order = 1/2

can exist!



He₂ bond order = 0

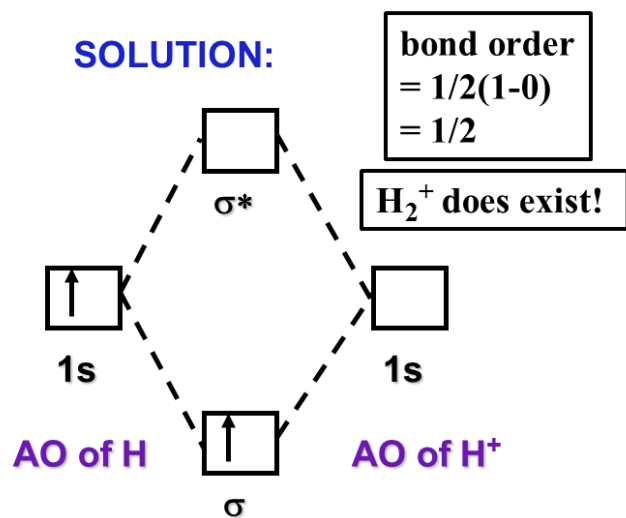
cannot exist!

SAMPLE PROBLEM 11.3 Predicting species stability using MO diagrams

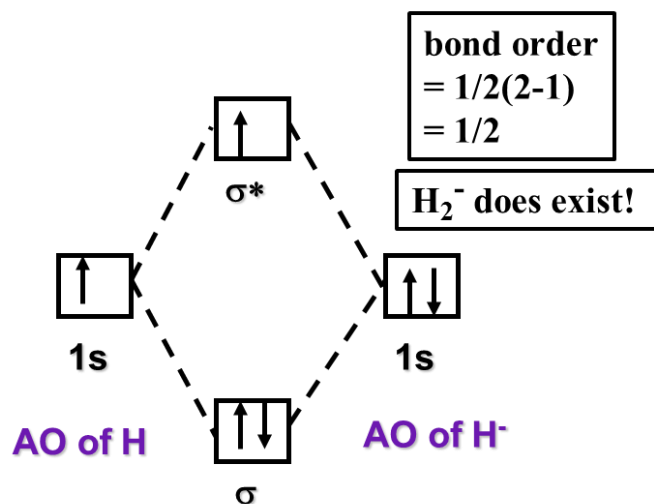
PROBLEM: Use MO diagrams to predict whether H_2^+ and H_2^- can exist. Determine their bond orders and electron configurations.

PLAN: Use H_2 as a model and accommodate the number of electrons in bonding and antibonding orbitals. Calculate the bond order.

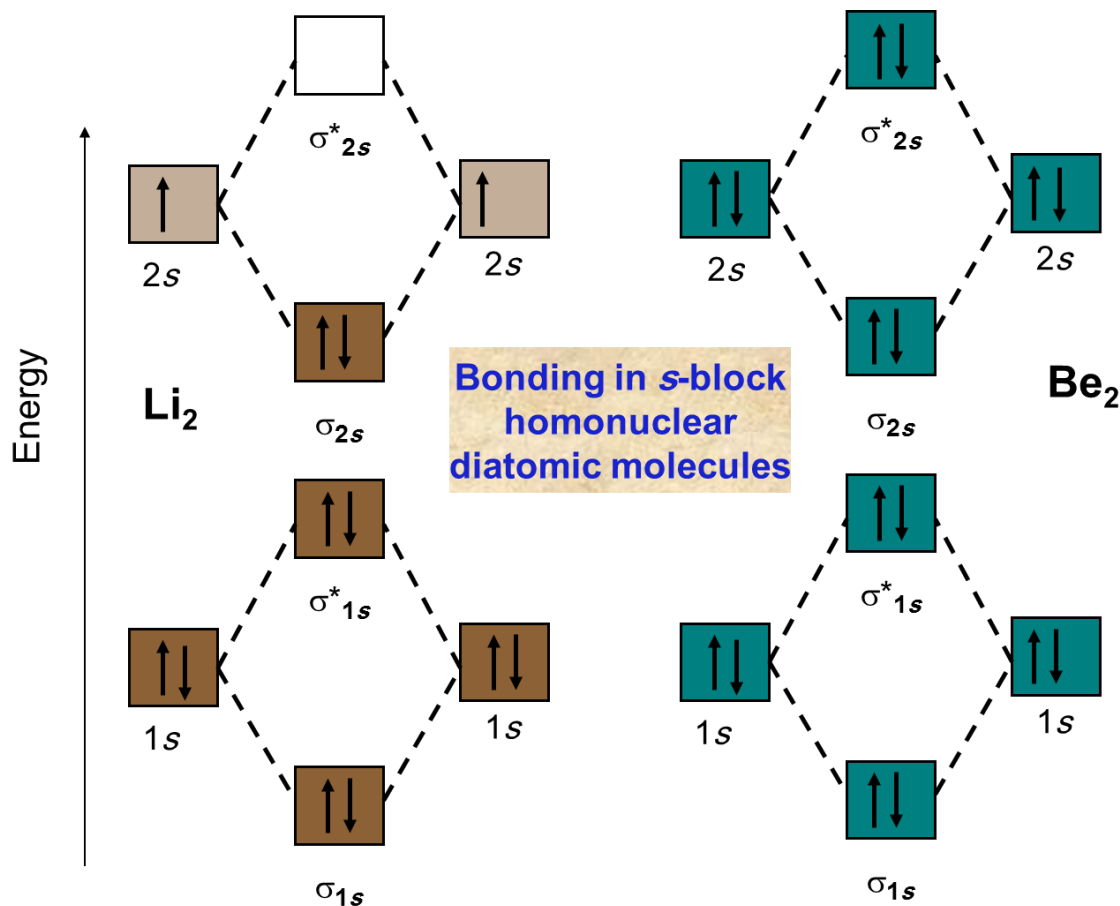
SOLUTION:



MO of H_2^+
configuration is $(\sigma_{1s})^1$



MO of H_2^-
configuration is $(\sigma_{1s})^2(\sigma_{1s}^*)^1$

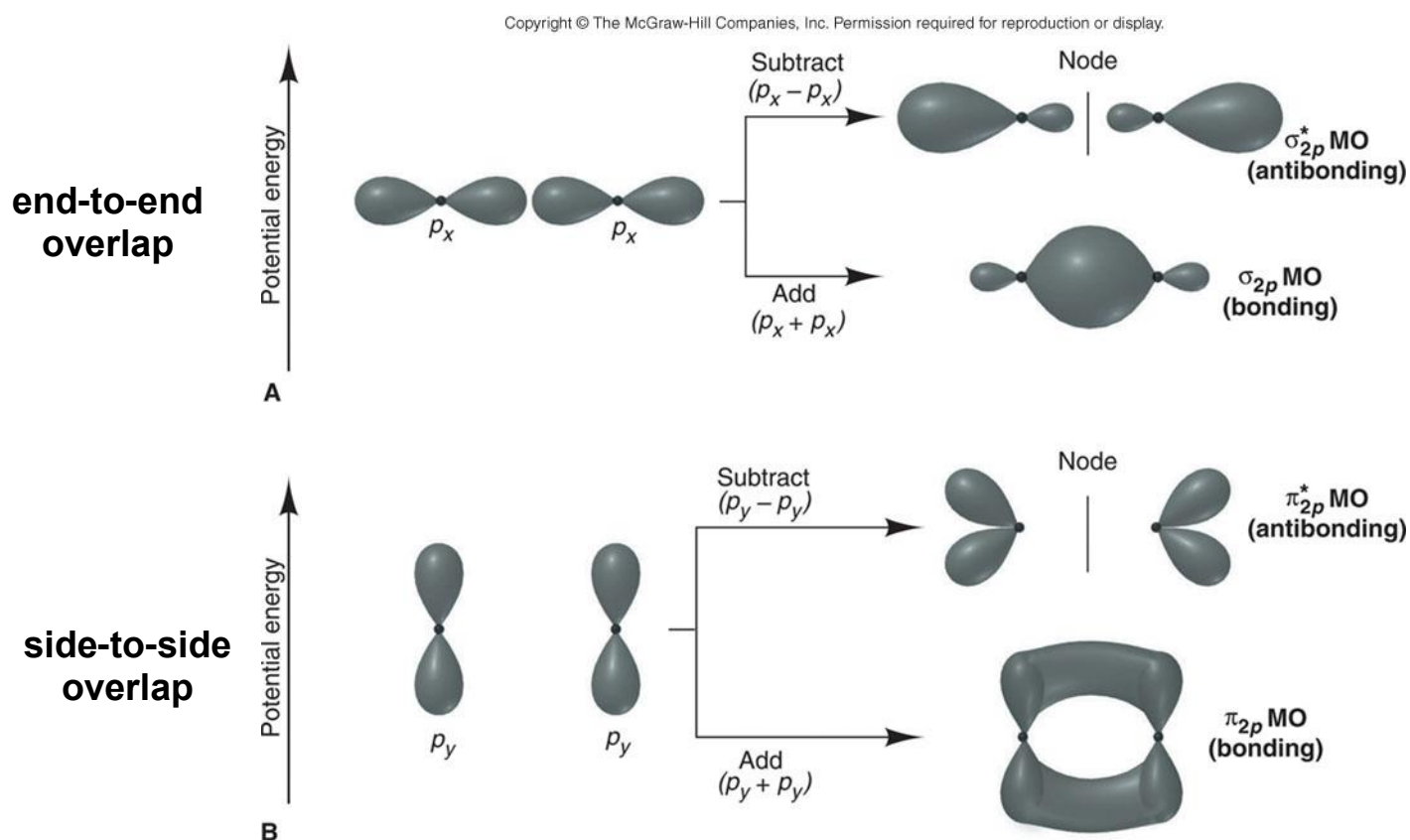


Li₂ bond order = 1

Be₂ bond order = 0

- Bonding and antibonding MOs for core electrons cancel = no net contribution to bonding .
- Only MO diagrams showing MOs created by combining valence-electron AOs are important.

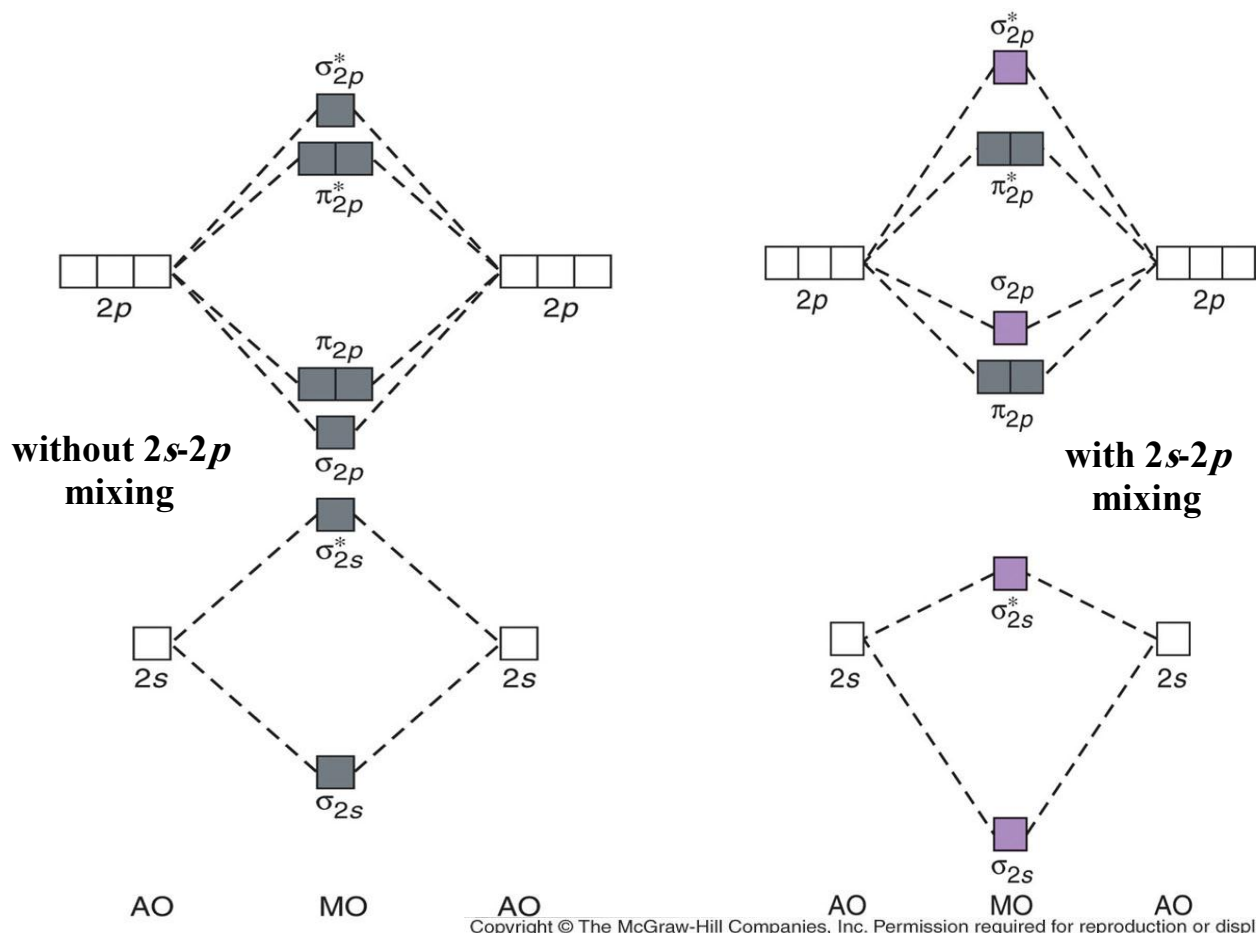
Contours and energies of σ and π MOs through combinations of $2p$ atomic orbitals



Relative energies

$$s_{2p} < p_{2p} < p_{2p}^* < s_{2p}^*$$

More effective end-to-end interaction relative to side-to-side in bonding MOs

Relative MO energy levels for Period 2 homonuclear diatomic moleculesMO energy levels for O_2 , F_2 and Ne_2 MO energy levels for B_2 , C_2 and N_2 **SAMPLE PROBLEM 11.4**

Using MO theory to explain bond properties

PROBLEM: As the following data show, removing an electron from N_2 forms an ion with a weaker, longer bond than in the parent molecule, whereas the ion formed from O_2 has a stronger, shorter bond.

	N_2	N_2^+	O_2	O_2^+
bond energy (kJ/mol)	945	841	498	623
bond length (pm)	110	112	121	112

Explain these facts with diagrams showing the sequence and occupancy of MOs.

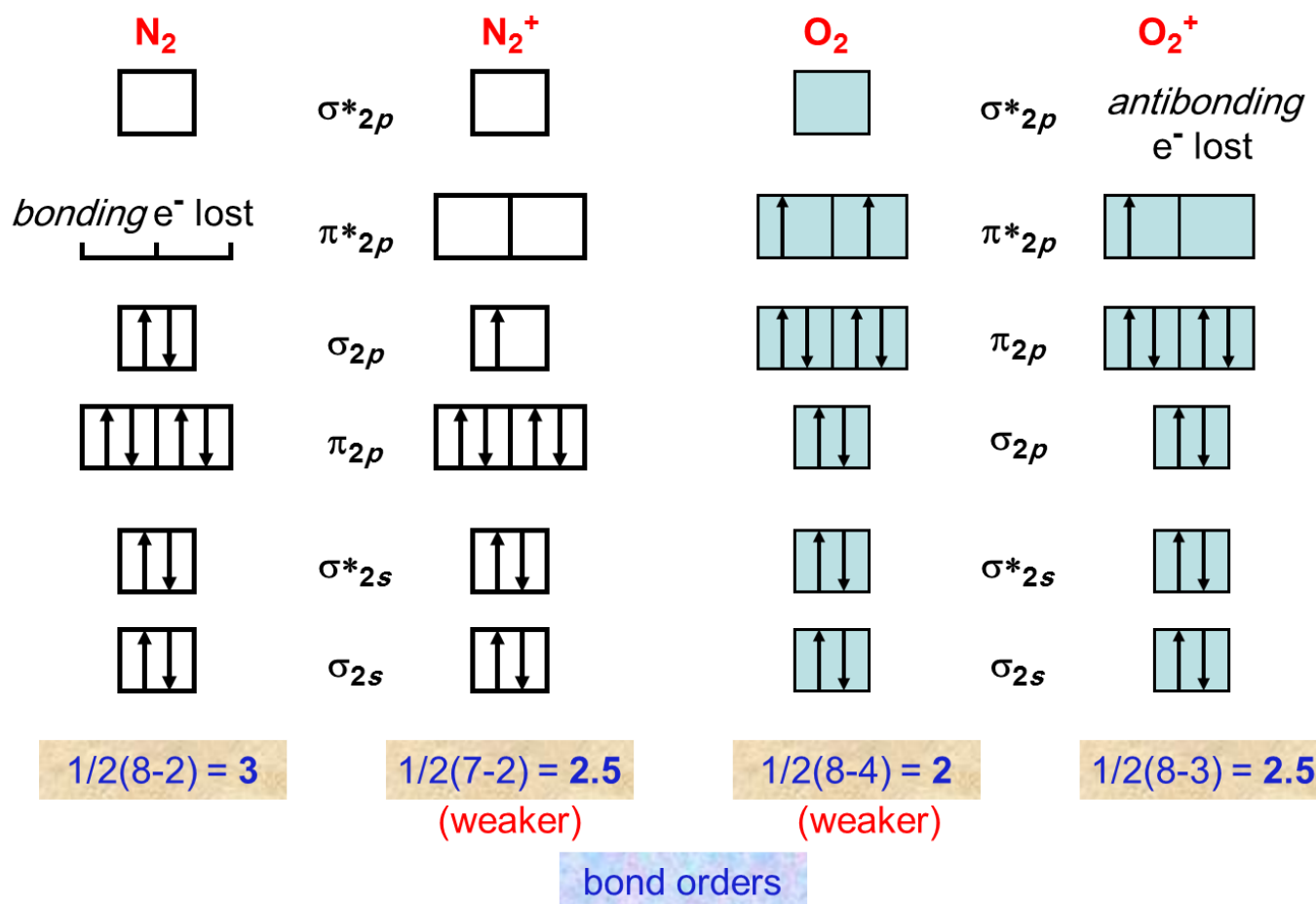
PLAN: Find the number of valence electrons for each species, draw the MO diagrams, calculate bond orders, and compare the results.

SOLUTION:

N_2 has 10 valence electrons, so N_2^+ has 9.

O_2 has 12 valence electrons, so O_2^+ has 11.

SAMPLE PROBLEM 11.4 (continued)



حصري # # #

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